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## Relating Extractable Soil Phosphorus to Phosphorus Losses in Runoff

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### ABSTRACT

Phosphorus in agricultural runoff can cause accelerated lake and stream eutrophication. Where producers have applied P at rates exceeding crop uptake, soil P has sometimes become the main source of P in runoff. We hypothesized that soil test P (STP) correlation to dissolved reactive P (DRP) and bioavailable P (BAP) in runoff varies, depending on the extraction method. To investigate which STP extraction method would be best for predicting DRP and BAP concentration and load in runoff, soil samples were taken from the 0- to 2-cm depth of 54 grass plots (5% slopes) on Captina silt loam (fine-silty, siliceous, mesic Typic Fragiudult). The STP was extracted by six methods and the ranges of results ( $\text{mg kg}^{-1}$ ) were: 54–490 (Mehlich III), 27–592 (Bray–Kurtz P1), 25–169 (Olsen), 14–110 (distilled water), 23–170 (Fe oxide paper), and 105–1131 (acidified ammonium oxalate). The soil P saturation ranged from 16 to 80%. Simulated rain was applied at  $100 \text{ mm h}^{-1}$  and runoff was collected for 30 min. The concentration of DRP in total runoff ranged from 0.31 to  $1.81 \text{ mg L}^{-1}$ , and BAP from 0.37 to  $2.18 \text{ mg L}^{-1}$ . The  $r^2$  values for STP by each extraction method correlated with runoff DRP and BAP, respectively, were: 0.72 and 0.72 (Mehlich III), 0.75 and 0.73 (Bray–Kurtz P1), 0.72 and 0.72 (Olsen), 0.82 and 0.82 (distilled water), 0.82 and 0.82 (iron oxide paper), 0.85 and 0.82 (acidified ammonium oxalate), and 0.77 and 0.76 (P-saturation). All correlations were significant ( $P < 0.001$ ), but the high  $r^2$  values of those obtained from distilled water, iron oxide paper, and acidified ammonium oxalate extractants indicate better precision for predicting DRP and BAP concentrations in runoff. Correlations of STP with DRP load (range: 43.4 to  $472.8 \text{ g ha}^{-1}$ ) and BAP load (54.2 to  $542.0 \text{ g ha}^{-1}$ ) were not useful ( $r^2 < 0.18$ ), possibly because runoff volumes were highly variable.

**S**URFACE RUNOFF from agricultural land is a contributor to accelerated eutrophication in lakes and streams. In recent reports to Congress, the U.S. Environmental Protection Agency identified agricultural nonpoint source (NPS) pollution as the major source of stream and lake contamination preventing attainment of the water quality goals identified in the Clean Water Act (U.S. Environmental Protection Agency, 1988).

Phosphorus and N are both nutrients often associated with accelerated eutrophication of lakes and streams

(Levine and Schindler, 1989). However, P is most often the element limiting accelerated eutrophication because many blue-green algae are able to utilize atmospheric  $\text{N}_2$ . Therefore, minimizing lake eutrophication from agricultural NPS pollution often requires controlling P inputs to surface water. The International Joint Commission between the U.S. and Canada recommended this approach for managing NPS pollution in the Great Lakes Basin (Rohlich and O'Connor, 1980). More recently, Florida NPS pollution programs have focused on P (Little, 1988). In the Netherlands, the national strategy for minimizing NPS pollution is to limit entry of P into both surface and groundwater (Breeuwsma and Silva, 1992). Recent review papers by Sharpley et al. (1994) and Daniel et al. (1994) also identified the importance of developing P management strategies to limit surface water eutrophication from agricultural NPS.

Sources of runoff P in an agricultural watershed are many and varied, but the greatest potential for accelerated eutrophication occurs with intense animal manure production (Duda and Finan, 1983). Manure is usually land applied and application rates are based on N needs of the crop, with little consideration given to crop P requirements. This practice often results in excessive P fertilization, because the P/N ratio found in manure is usually much higher than the P/N ratio required by plants. For instance, when manure was used to meet N needs for fescue (*Festuca arundinacea* Schreber) production in northwest Arkansas, an excess of 40, 37, and  $17 \text{ kg ha}^{-1}$  of P was applied annually using poultry, swine, or dairy manure, respectively (Huneycutt et al., 1988; American Society of Agricultural Engineers, 1991; Soil Conservation Service, 1992). The P excesses were greater when application rates were increased to compensate for N losses (e.g., volatilization). Thus, the inherent characteristics of animal manures and nutrient uptake of crops can promote P buildup in soils.

Long-term nutrient application at rates exceeding crop uptake can elevate STP levels in areas of intensive crop and livestock production. For example, 65% of soils tested in Delaware were in the high to excessive P range (Sims, 1992). In an intensive poultry production area of Arkansas, Mehlich III soil tests showed that in 1992

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>63% of soils from Benton and Washington counties were high in STP (above 50 mg kg<sup>-1</sup>) and 28% were very high (above 150 mg kg<sup>-1</sup>) (Snyder et al., 1993).

Previous research indicated that P content of surface soil directly influences the amount of DRP in runoff from that soil (Sharpley et al., 1977, 1978, 1994; Daniel et al., 1994). Because STP and runoff DRP concentrations are related, excessive STP levels may result in runoff sufficiently high in DRP to accelerate eutrophication of P-limited aquatic systems. This link must be considered in developing P management strategies that limit eutrophication but sustain high crop production. In fact, the ubiquitous contribution of runoff P from soils with elevated STP levels is potentially a more important and difficult to manage source of DRP than improper land application of manure. In fescue-pasture watersheds where STP (Mehlich III) was above 150 mg kg<sup>-1</sup>, mean annual P concentrations in natural runoff ranged from 1.25 to 2.60 mg L<sup>-1</sup>, with elevated STP levels responsible for 65 to 90% of annual P loss even when a major runoff event occurred 1 d after manure application (Edwards et al., 1993). The residual nature of STP makes this source of runoff P especially problematic.

Lacking clear eutrophication standards and research data, some states (OH, MI, WI, and AR) have used a subjective process, based on STP levels adequate for crop production and those "perceived" to bring about eutrophic runoff, to identify a general threshold STP level for management purposes (Sims, 1992). Unfortunately, no research base exists that relates these threshold levels directly to runoff water quality.

A study was conducted to begin developing a research base for best management practices related to STP levels in northwestern Arkansas. At present, routine soil tests for P are only designed to estimate the P fertility status of soils for crop production, not their potential for release of P to surface water (Miller et al., 1993). We hypothesized that STP correlation to DRP and BAP in runoff varies, depending on the extraction method. Therefore, our objective was to determine which STP extraction method would be most useful for predicting DRP and BAP concentration and load in runoff from Captina silt loam.

## MATERIALS AND METHODS

The 54 plots used for this study were constructed at Fayetteville, AR, on a Captina silt loam in the fall of 1990. The surface soil had a pH of 5.0, approximately 1.3 g cm<sup>-3</sup> bulk density, 11 g kg<sup>-1</sup> organic matter content, and particle-size distribution of 23% sand, 69% silt, and 8% clay. Each plot was 1.5 by 6 m with a uniform slope of approximately 5%, borders to isolate plot runoff, and a flow collector as described by Edwards and Daniel (1993).

Fescue was established in the plots at the time they were constructed, and has been continuously maintained. At the time of our study (fall of 1993), all of the plots had a dense stand of fescue that provided virtually uniform 100% ground cover and a thick layer of thatch material. Fescue is the most common crop and Captina silt loam is representative of soils in northwestern Arkansas that regularly receive surface applications of poultry manure, resulting in high levels of STP.

These plots provided a wide range of STP levels because they were previously used to investigate water-quality effects of pasture fertilization with swine and poultry manure. They had received surface applications of swine, broiler, or caged layer manure to furnish 0, 220, 440, or 880 kg N ha<sup>-1</sup> in 1991, with treatments assigned to plots in a randomized complete block design. These manure application rates supplied 0, 19, 38, 54, 76, 108, 215, or 304 kg P ha<sup>-1</sup>, depending on the type of manure and the application rate. Some had also received manure (swine, broiler, or caged layer), or commercial inorganic fertilizer to supply 220 kg N ha<sup>-1</sup> and 87 kg P ha<sup>-1</sup> in 1992. However, at the time of our study, none of the plots had nutrient applications during the previous year. Thus, the amendments had more than a year to decompose and equilibrate in the soil prior to our simulated rainfall.

Soil cores for this study were taken only from the top layer of soil (0–2-cm depth), based on work by Sharpley et al. (1978). A representative soil sample was collected from each plot on Sept. 1993, just before the simulated rainfall application, and consisted of a composite of 10 cores (2.54-cm diameter) taken randomly from the plot surface. This provided adequate soil for analysis with minimal damage to the plot surface. Each soil sample was air dried and sieved (2 mm), thus removing larger rock particles and most of the grass thatch material.

To reduce runoff variability due to antecedent moisture conditions, the plots were saturated by low-intensity irrigation and allowed to drain for 48 h prior to our simulated rainfall. A simulator described by Edwards et al. (1992) generated 30 min of runoff from each plot by applying simulated rain at an intensity of 100 mm h<sup>-1</sup>.

Runoff samples were taken manually at 5-min intervals during the runoff event. The sample volume and time required to collect it were recorded and used to calculate the mean flow rate and total runoff volume for the 5-min interval. A subsample was filtered (0.45- $\mu$ m pore diameter) in the field to remove particulate matter. All soil and runoff samples were stored in the dark at 4°C until analyzed.

Extractable P in each soil sample was determined using six different methods: Mehlich III (Mehlich, 1984), Bray-Kurtz P1 (Bray and Kurtz, 1945), Olsen (Olsen et al., 1954), Fe oxide impregnated paper strip (Sharpley, 1993), distilled water, and acidified ammonium oxalate. At present, the Mehlich III, Bray-Kurtz P1, and Olsen chemical extractants are commonly used for STP analysis in soil testing laboratories. These methods were developed to assess the fertility status of soil for crop production, not to predict runoff water quality. Experiments have shown that P reacting with Fe oxide coated filter paper closely approximates P actually available to growing algae (BAP) (Sharpley, 1993). Therefore, this method may give the best estimate of the potential for accelerated eutrophication from elevated P levels in soils. Distilled water dissolves less P than the other STP extractants, but may be the most appropriate for predicting runoff DRP. One gram of soil was mixed with 25 mL of distilled water, shaken end-over-end for 1 h, centrifuged for 5 min at 266 m s<sup>-1</sup> (27 100 g), filtered (0.45  $\mu$ m), and the supernatant analyzed for P by the molybdenum-blue method (Murphy and Riley, 1962). Acidified ammonium oxalate dissolves noncrystalline oxides of Fe and Al (the compounds to which most phosphate adsorbs in acid soils), releasing into solution the phosphate that may eventually be desorbed. Ammonium oxalate extractant (Sheldrick, 1984) was made by mixing 0.2 M oxalic acid with 0.2 M ammonium oxalate (approximately 535 mL of oxalic acid with 700 mL of ammonium oxalate) until the combined-solution pH was 3.0. A 20-mL aliquot of the ammonium oxalate solution was then mixed with 0.5 g of soil, shaken in the dark for 2 h,

Table 1. Results (range and mean) of various soil test P (STP) methods from 54 Captina plots.

STP method	STP	
	STP range	Mean
	mg kg <sup>-1</sup>	
Mehlich III	54–490	198
Bray-Kurtz P1	27–592	231
Olsen	25–169	81
Distilled H <sub>2</sub> O	14–110	61
Ammonium oxalate	105–1131	503
Fe <sub>2</sub> O <sub>3</sub> paper	23–170	92

centrifuged for 20 min at 131 m s<sup>-1</sup> (14 481 g), and decanted for P analysis.

Runoff DRP was quantified by the molybdenum-blue method for P in water samples (Murphy and Riley, 1962), and BAP was quantified by the Fe oxide impregnated paper strip method (Sharpley, 1993). The mean DRP and BAP concentration in each plot's runoff was determined by using concentration and flow rate to calculate a flow-weighted mean concentration. Total DRP and BAP mass losses (loads) from each plot during the runoff event were calculated by multiplying the flow-weighted mean P concentration by the plot's total runoff volume.

All of the STP methods were statistically compared by correlating STP results to DRP and BAP concentrations in runoff from the plots, developing a linear regression, and calculating the correlation coefficient for each. We then determined which STP method correlated most closely (had the highest correlation coefficient) with DRP and BAP concentrations in runoff.

The P saturation of each soil sample was calculated as the oxalate-extractable P (mmol kg<sup>-1</sup>) divided by the oxalate-extractable Al and Fe (mmol kg<sup>-1</sup>) content, and multiplied by 100. The P saturation (%) was then correlated to DRP and BAP runoff levels.

## RESULTS AND DISCUSSION

The mean rainfall application required to produce 30 min of continuous runoff was 62.5 mm (CV = 9.7%). The total surface runoff from each plot ranged from a low of 4.6 mm to a high of 47.6 mm, with a mean of 27.0 mm (CV = 40.4%). The runoff variability was probably related to differences in infiltration rate, especially macropore flow. As the runoff event progressed, increasing soil water content beneath the surface layer reduced the infiltration rate and the amount of runoff increased steadily, from a mean of 2.6 mm during the first 5-min interval to 5.4 mm during the last 5 min of runoff.

The average DRP concentration in runoff from all of

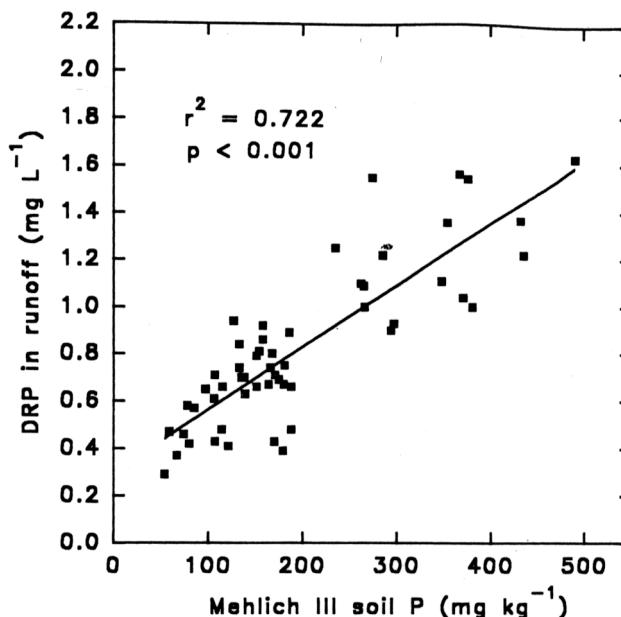


Fig. 1. Relationship between Mehlich III extractable P in Captina surface soil and dissolved reactive P (DRP) in runoff.

the plots declined steadily during the runoff event, from 1.73 mg L<sup>-1</sup> during the first 5 min to 0.50 mg L<sup>-1</sup> during the last 5 min. This decline was attributed primarily to the dilution effect of increasing runoff volumes, including some water that never came in direct contact with the soil surface. Also, some decline in the DRP concentration may have occurred as the DRP already in the soil solution was eluted out early in the runoff event. The mean DRP concentration for the entire runoff event from each plot ranged from a low of 0.31 mg L<sup>-1</sup> to a high of 1.81 mg L<sup>-1</sup>. The BAP runoff concentration was slightly higher than DRP, ranging from 0.37 to 2.18 mg L<sup>-1</sup>.

The mean and range of STP values obtained for the 54 plots using each STP method are shown in Table 1. The *r*<sup>2</sup> value, slope, and y intercept for each STP correlation to DRP and BAP in runoff are given in Table 2. The STP values obtained by all of the extraction methods were significantly (*P* < 0.001) correlated to DRP and BAP concentrations in plot runoff. The STP values obtained from conventional soil testing laboratory extractions, Mehlich III (Fig. 1), Bray-Kurtz P1, and Olsen methods, all had similar *r*<sup>2</sup> values (Table 2). However, the highest correlations to DRP and BAP levels in runoff were obtained when STP was extracted by distilled water (Fig. 2), acidified ammonium oxalate, or Fe oxide paper strip (Table 2). Since water is the solvent for P in

Table 2. Results of various soil test P (STP) methods correlated to dissolved reactive P (DRP) and bioavailable P (BAP) in runoff.

Soil P (mg kg <sup>-1</sup> ) STP method	Correlation to DRP (mg L <sup>-1</sup> )			Correlation to BAP (mg L <sup>-1</sup> )		
	<i>r</i> <sup>2</sup>	slope	y intercept	<i>r</i> <sup>2</sup>	slope	y intercept
Mehlich III	0.722	0.0026	0.30	0.717	0.0030	0.39
Bray-Kurtz P1	0.748	0.0022	0.31	0.729	0.0025	0.41
Olsen	0.718	0.0088	0.11	0.717	0.0102	0.17
Distilled H <sub>2</sub> O	0.824	0.0118	0.10	0.815	0.0136	0.16
NH <sub>4</sub> -oxalate	0.848	0.0013	0.19	0.824	0.0014	0.27
Fe <sub>2</sub> O <sub>3</sub> paper	0.819	0.0077	0.10	0.822	0.0090	0.16

† All *r*<sup>2</sup> values were significant at *P* < 0.001.

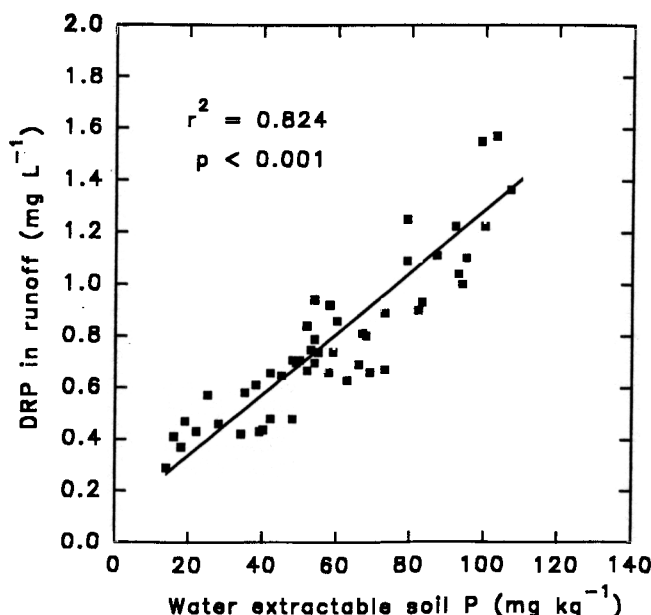


Fig. 2. Relationship between water-extractable P in Captina surface soil and dissolved reactive P (DRP) in runoff.

the runoff, we had hoped that the distilled water STP extractant would be even more highly correlated to DRP in runoff than was observed in this study. Also, since BAP was extracted by Fe oxide paper in both runoff and soil, a higher correlation between soil BAP and runoff BAP might be expected. However, in addition to STP, runoff DRP levels are dependent on other variables such as total runoff amount and depth to which runoff interacts in the soil (Sharpley et al., 1993).

The DRP concentration was consistently between 72 and 94% of the BAP concentration in each of the runoff samples, with a mean of 83% for all of the samples. Since BAP concentrations in runoff were only slightly

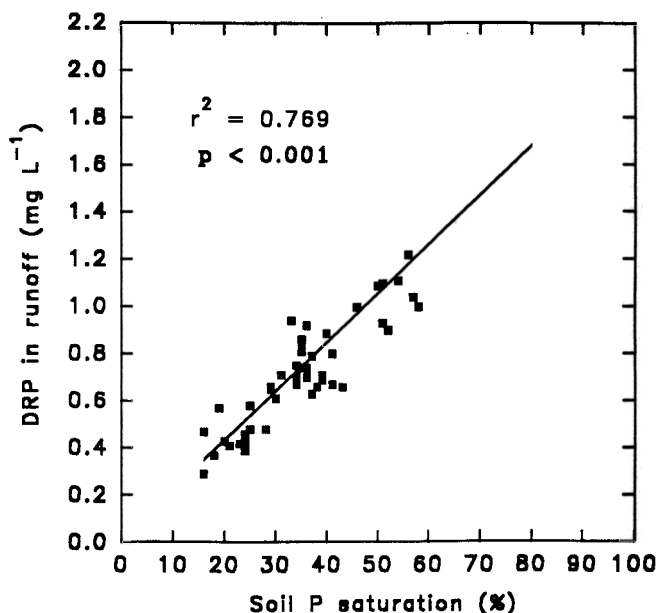


Fig. 3. Relationship between P saturation of Captina surface soil and dissolved reactive P (DRP) in runoff.

higher than DRP concentrations, it is not surprising that BAP correlations to STP were similar to those obtained for DRP, and also highly significant ( $P < 0.001$ ; Table 2).

A link has been suggested (Breeuwsma and Silva, 1992) between the P concentration in soil solution and the extent to which the soil is saturated with P, so P concentration in runoff may also be related to P saturation of the soil. Previous research has shown that the P-sorption capacity of low-pH soil is primarily due to its oxalate-extractable Al and Fe content (Breeuwsma and Silva, 1992). Based on this, the P saturation of our plots ranged from 16 to 80% (mean was 39%), and showed significant ( $P < 0.001$ ) correlation to DRP (Fig. 3) and BAP ( $r^2 = 0.756$ , slope = 0.0238, intercept = 0.07) in plot runoff. However, we do not know whether these correlations would hold true for soils other than Captina silt loam.

The DRP mass loss (load) during the runoff ranged from 43.4 to 472.8 g ha<sup>-1</sup>, and BAP mass loss ranged from 54.2 to 542.0 g ha<sup>-1</sup>. Large differences in infiltration rate resulted in highly variable runoff volumes among the plots. Therefore, although the concentration of both DRP and BAP in runoff showed good correlation to STP, the P load in the runoff did not correlate well with STP, whether measured as DRP (Fig. 4) or BAP ( $r^2 = 0.143$ ,  $P < 0.01$ ).

## CONCLUSIONS

The results of this study provide further evidence of a linear relationship between STP levels and DRP (or BAP) concentration in runoff from the soil surface. When soil samples were taken only from the surface layer of soil (0–2-cm deep), a linear relationship was apparent (significant at  $P < 0.001$ ) regardless of which STP method was used. However, STP correlated best to runoff P

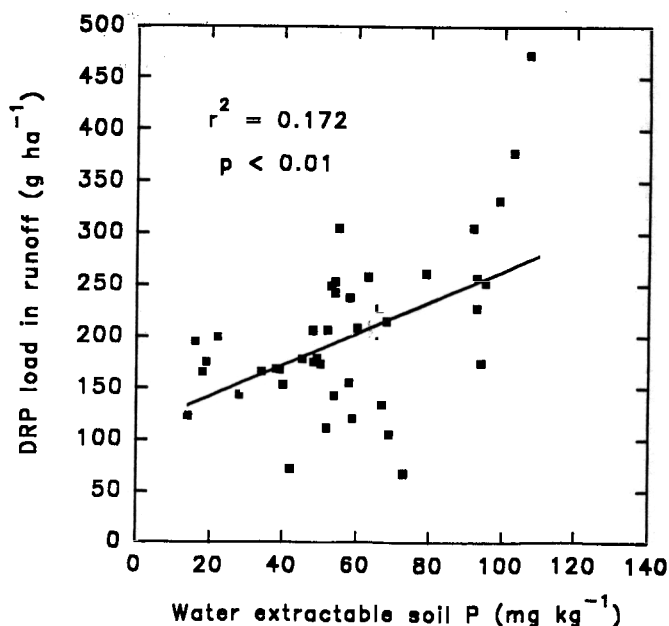


Fig. 4. Relationship between water-extractable P in Captina surface soil and dissolved reactive P (DRP) load in runoff.

when the STP was extracted with distilled water, acidified ammonium oxalate, or Fe oxide paper strips. The form of P extracted (DRP or BAP) from runoff had very little, if any, effect on the correlation between STP and runoff P.

Although distilled water, acidified ammonium oxalate, and Fe oxide paper strips were the most effective STP extractants used in this study to predict DRP and BAP concentrations in runoff, time or economic constraints may sometimes require the use of the less effective Mehlich III, Bray-Kurtz P1, or Olsen STP methods to make such predictions.

The P saturation status of the soil in this study was significantly ( $P < 0.001$ ) related to DRP and BAP concentrations in the runoff. Further research is needed to determine whether this relationship is similar enough in other soils to be valuable as a universal predictor of DRP and BAP concentrations in runoff.

The DRP concentrations in runoff from all plots declined as flow rates increased during the runoff event. Although correlations of STP to DRP and BAP loads were significant at  $P < 0.01$ , the  $r^2$  values were low because total runoff amounts varied greatly among plots. Therefore, these correlations would not be very useful for predicting DRP and BAP loads. However, if other studies can find a method for accurate prediction of runoff volumes, STP analyses could yet be valuable for predicting total DRP or BAP loads.

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